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Review of catalytic supercritical water gasification for hydrogen production from biomass

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ABSTRACT

Hydrogen is defined as an attractive energy carrier due to its potentially higher energy efficiency and low generation of pollutants, which can replace conventional fossil fuels in the future. The governments have invested huge funds and made great efforts on the research of hydrogen production. Among the various options, supercritical water gasification (SCWG) is a most promising method of hydrogen production from biomass. Supercritical water (SCW) has received a great deal of attention as a most suitable reaction medium for biomass gasification because it is safe, non-toxic, readily available, inexpensive and environmentally benign. However, high temperature and pressure are required to meet the minimum reaction condition. Therefore, the high operating cost has become the biggest obstacle to the development of this technology. To overcome this bottleneck, many researchers have carried out intensive research work on the catalytic supercritical water gasification (CSCWG). Based on the previous studies stated in the literature, the authors try to give an overview (but not an exhaustive review) on the recent investigations of CSCWG. Besides, the physicochemical properties of SCW and its contributions in subcritical and supercritical water reaction are also summarized.

Contents

1. Introduction

Energy shortage and environmental pollution are two difficult problems we have to deal with in the future. With the increasing consumption of fossil fuels, the reserves cannot be restored via positive and feasible ways because of its non-renewability. Among the many options, hydrogen, as a renewable and green alternative energy sources, has been attracted extensive attention worldwide. It can be not only used for machinery with zero emission, but also for high thermal efficient hydrogen fuel cells. It acts in accord with increased regulatory environmental protection policies, so the research of hydrogen is becoming prevalent in many countries.

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In general, conventional hydrogen production methods and their shortcomings can be classified as follows:

(i) Electrolysis of water, the production cost is too high.
(ii) Water photolysis, under laboratory studies at present.
(iii) Thermal pyrolysis and reforming of organic compounds, moisture content must be limited during the hydrogen production, so the dehydration process is necessary for the pretreatment of wet feed.
(iv) Hydrogen production via methanation of microorganism, reaction rate is slow and conversion efficiency is low.

Compared with the conventional methods above, SCWG process is characterized by its high reaction efficiency and H_2 selectivity. It adopts water as reaction medium and can be fed by high moisture content material. Among many hydrogen production methods by bioconversion, many researchers believe that SCWG is one of the hydrogen production methods with great potentiality [1,2].

However, SCW reactions have deficiencies like poor material compatibility and need for high temperature and pressure. Product distribution of SCWG process, to a large extent, depends on operation conditions. The early investigation found that high yield of hydrogen can be obtained only under the condition that the temperature is higher than 600 °C [4,5]. At low temperatures (<450 °C), CH_4 is major product. When the water density enhances, the methane yield increases and hydrogen yield reduces. Different from many exothermic reactions, SCWG process cannot maintain the minimum temperature that the reaction needs through self-sufficiency. So the economical efficiency has become the greatest obstacle to the further development of SCWG [3].

In order to moderate violent reaction conditions, and to reduce equipment investment and operating cost, one of available means is to reduce activation energy by adding suitable hydrothermal catalyst. Consequently, the research of catalyst which applies to hydrothermal condition is of vital importance to this technique. Catalytic supercritical water gasification (CSCWG) will certainly become an important research direction in this field.

2. Supercritical water

2.1. Thermophysical property of SCW

When water temperature and pressure reach its critical point ($T_c \geq 374$°C, $P_c \geq 22.1$ MPa), a new state can be found—supercritical state. Physicochemical characteristics such as ion product, density, dielectric constant and viscosity of water, under supercritical conditions, are greatly different from either extreme state of the gas phase or the liquid phase.

Hydrogen bond is an important factor to reflect the difference between macroscopic and microscopic properties of water. Temperature increment can change or destroy the chemical structure of water in room temperature. At normal temperature and pressure, dielectric constant is comparatively large (approximately 80) because of strong effect of hydrogen bond in water. Nevertheless, as temperature and pressure increase, dielectric constant of water declines sharply (further to 5 at critical point).

The change of dielectric constant can lead to the change of dissolving capacity of water. Dielectric constant of supercritical water is roughly corresponding to that of common organic compounds. It can perform similarly to nonpolar organic compounds, so the good solubility makes it a solvent for nonpolar organic compounds. On the contrary, dissolving capacity for high polar inorganic compounds drops dramatically, which cause separation of dissolved organic compounds out of water.

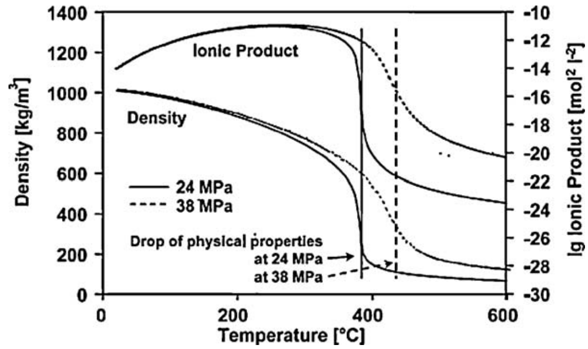


Fig. 1. Physical properties of HTW at different pressures [6].

Increment of temperature can also cause the change of water viscosity. At critical point, viscosity of water (2.98×10^{-5} Pa s) is close to that of vapor (2×10^{-5} Pa s). Lower viscosity can provide a high diffusion coefficient for water, which in turn can create a perfect reaction condition for high reaction rate.

As can be seen from Fig. 1, near the critical point, the density and ion product of water are lower than those of normal condition. The density varies from liquid (1 g/cm^3) to low-pressure vapor (<0.0011 g/cm^3) with temperature and pressure. Ion product is related to both temperature and density, but density has greater impact. The higher the density is, below critical point, the higher the ion product is. In such a case, the ionic reaction mechanism is preferable. On the other hand, the decrease of water density causes the drop of ion product because the increment of temperature is above critical point, which indicates that free-radical mechanism is preferable in this situation [30].

The reaction in supercritical water has many advantages over conventional gaseous and liquid reaction methods:

(i) High reaction rate, gaseous product with high concentrations can be obtained [1].
(ii) As there is no limit of interphase mass transfer resistance that exists in conventional reaction system, the reactions proceed very rapidly and completely [7].
(iii) There is a possibility of convenient post-reaction separation of water and products simply by change the operating parameters such as temperature and pressure. It would be more favorable to the separation of product than distillation or extraction [8,9].
(iv) Higher dispersivity and better heat transfer characteristic are provided in the reaction process than that those in gas and liquid [10].
(v) Good flowability and carrying capacity of SCW can decrease the yield of coke, thus prolong the service life of the catalyst [2,11–14].

Therefore, supercritical water has been widely regarded as an attractive and potential reaction medium owing to its unique nature and the sound environmental compatibility.

2.2. Role of water in the reaction

The structure of high temperature water (HTW, water at temperatures exceeding the normal boiling point) is different from that of normal temperature water, especially in supercritical state. As described above, ion product of supercritical water is two orders of magnitude higher than that at ambient temperature. High concentration of H^+ and OH^- can be obtained in SCW, and it is possible to provide a perfect environment for acid- or base-catalyzed reaction [6]. SCWG is a process associated with

hydrolysis and pyrolysis reaction [14]. Water not only as a reactant involved in the reaction, but also as a catalyst has a significant impact on the SCWG reaction process. Hence, understanding of the contributions of water in SCW reaction is indispensable to the research of homogeneous or heterogeneous catalytic mechanism.

2.2.1. Water as a participant in reaction

2.2.1.1. Contributions in hydrolysis reaction. HTW or SCW, not only as a reaction medium but also as a reactant takes part in the reaction. In hydrolysis reaction, water and salt can produce acid or alkali which has influence on bond scission of organic compounds. Many experiments which were based on model compounds were conducted to test this effect of water in SCW or HTW reaction. Ogunsola et al. [15] suggested that the protons provided by SCW can promote the saturation of heterocycle and the formation of alkyl and C–N radical. Interaction with SCW or HTW can accelerate the elimination of S and ring opening of heterocycle compare with normal hydrolysis.

Several researchers [16,17] have reported that conversion of amines and amides is the combination of pyrolysis and hydrolysis. Pyrolysis mechanism is more preferable at high temperature and hydrolysis mechanism is more preferable in case of high water density. In addition, reaction of organic compounds in subcritical water can be reinforced by autocatalysis of hydrolysate [18,19], because acid and alkali generated in the process of hydrolysis may cause the catalytic effect on the reaction pathway.

2.2.1.2. Resource of hydrogen. Water structure is changed at high temperature condition, which leads to the slacking down of intramolecular and intermolecular hydrogen bonding. It makes the water possible to provide hydrogen. In order to prove the capacity of HTW to provide hydrogen, a research was conducted by using D_2O instead of H_2O as a reaction medium in the hydrothermal reaction of hydrocarbons and found that the hydrogen–deuterium exchange existed in the process and part of the deuterium atoms entered into the product [20]. Park et al. [21] used D_2O instead of H_2O as a reaction medium for the SCWG of some organic compounds with RuO_2 catalyst. They found that the methane and hydrogen in gas production are not CHD3, H2 or HD, but CD4 and D2, which indicated that all the H in gas product is from water. The reaction mechanism is demonstrated in Fig. 2.

This capacity of water to provide hydrogen makes it a significant influence on distribution of pyrolytic production. Hydrogenation plays a role of chain termination in free-radical chemistry, which can reduce the molecular weight of organic compounds such as polymer to form a large number of small molecule compounds. Watanabe et al. [22] found that the HTW can reduce coking and restrain the formation of condensation product in the experiment of polyethylene hydrolysis in SCW. Kruse et al. [23] investigated the SCWG of catechol and found that the increase of H_2 yield is in proportion to the contribution of H_2O in the reaction process. By contrast, the increased concentration of catechol (means that the reduction of water concentration) is inversely proportional to H_2 production. It is indicated that the water molecules release hydrogen atoms to accelerate the intramolecular bond rupture of reactant.

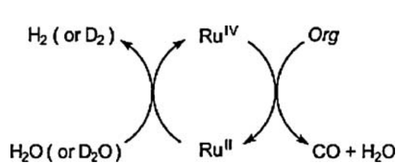


Fig. 2. SCW-induced redox cycle between Ru^{IV} and Ru^{II} catalyzing the gasification of organic compounds [21].

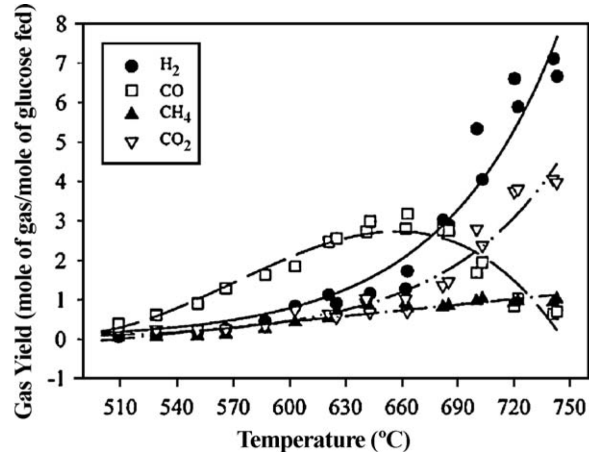


Fig. 3. Variation of product distribution with reactor temperature in supercritical water gasification (glucose 0.6 M pressure 28 MPa and reactor residence time 30 s) [25].

In addition to this, water can also produce H_2 through the water-gas shift reaction. A large number of reports have confirmed the existence of this phenomenon:

$$CO + H_2O \rightleftharpoons CO_2 + H_2, \quad \Delta H = -41\ \text{kJ/mol} \tag{1}$$

This reaction is weakly exothermic and thermodynamically limited at operational temperatures of the process, but allows a significant CO abatement and a further hydrogen formation [24]. Lee et al. [25] studied SCWG of glucose without catalyst (480–750 °C, 28 MPa, 10–50 s), they observed that CO yield is high in early stage of conversion. When the temperature is over 650 °C, as shown in Fig. 3, CO concentration decreases and H_2 production enhances because of the beginning of water-gas shift reaction. Byrd et al. [26] conducted an investigation on SCWG of glycerol and found that CO yield is lower than prospective equilibrium value while H_2 yield is higher than prospective equilibrium value. It is indicated that the water-gas shift reaction occurs in late stage of the process with Ru/Al_2O_3 catalyst.

2.2.1.3. Resource of free-radicals. Free-radical mechanism dominates the conversion of organic compounds at high temperature, which is composed of two phases: an induction period (the generation of a radical pool) and a fast free-radical reaction period. The both steps play an important role in reaction kinetics. The induction time and free-radical concentration depend on temperature, catalysts and reactants [28]. In general, temperature has a great influence on the induction period. Al-Duri et al. [29] reported the induction time is 3.6 s and 1.5 s at 400 °C and 450 °C in the investigation of high temperature degradation of nitrogen compounds, respectively. The conclusion indicates that free-radical formation is temperature controllable.

Low water density is preferred for the free-radical reaction. Henrikson et al. [30] noted that different water density may accelerate or inhibit supercritical water reaction at the same temperature. One possibility is that water can accelerate the reaction depends on ionic reaction mechanism at high water density, but on free-radical mechanism at low water density.

H and OH generated from SCW ionization can promote the heterolytic reaction of aromatic compounds. At the same time, the coupling reaction is also suppressed in the process. With the replacement of hydroxyl groups, π-electrons become delocalized, which causes the instability of benzene ring. Further substitution and attack lead to the ring cleavage reaction and generating a relatively low-molecular weight compounds [28].

Hydroxyl radical is considered to be the most important and effective oxidant in SCW reaction. In many cases, the formation of hydroxyl radical is a control step of overall reaction kinetics. Dagaut et al. [31] built a complete set of free-radical reaction kinetic model of methanol using tubular flow plug reactor under supercritical water oxidation condition. They suggested that the reaction kinetic of methanol is controlled by the formation and decomposition of H_2O_2. Because the H_2O_2 can be decomposed to hydroxyl radical which controls the consumption of methanol. Savage et al. [32] also reported that the formation of hydroxyl radical is a control step in supercritical water oxidation reaction kinetics of methane.

2.2.2. Water as a catalyst

Water molecules also participate in SCW reaction as a catalyst. SCW can knock off H^+ and OH^- with high concentration, which creates a perfect condition favorable to acid–base catalytic reactions [33–35].

2.2.2.1. Contribution in acid catalytic reactions. Acid catalyzed reaction of the organic compounds is available in the pure subcritical and supercritical water without any catalyst. Kuhlmann et al. [36] reported that dehydration of cyclohexene occurs at subcritical condition without addition of catalyst. They supposed that the reaction was catalyzed by H_3O^+ generated from water at high temperature. This hypothesis is in consistent with the research by Xu et al. [37], who noted that the reaction of *tert*-butyl alcohol occurs at 250 °C in water without addition of any catalyst. The catalytic reaction mechanism scheme is shown in Fig. 4.

Chandler et al. [38] found Friedel–Craft alkylated reaction occurs in subcritical Water without catalyst. Temperature has great influence on the ionization of water. Water can be an effective acid catalyst at subcritical condition. In addition, Ikushima et al. [34] reported that SCW itself successfully functions as an acid catalyst in accelerating pinacol and Beckmann rearrangements.

2.2.2.2. Contribution in base catalyzed reactions. In SCW, many chemical reactions take place, which, under normal conditions, were previously only possible with the addition of base catalyzed materials. To testify the base catalytic effect of supercritical water, Ikushima et al. [35] conducted an investigation on benzaldehyde disproportionation without catalyst. The postulated mechanism scheme is shown in Fig. 5. The OH^- ion is required to form the product alcohol in any reaction mechanisms, and the participation of the OH^- ion in the disproportionation using SCW is clearly demonstrated.

Ethanol and formic acid can be produced from Cannizzaro-type reactions of formaldehyde in subcritical water without catalyst, which is well-known to occur in the presence of a large amount of base catalyst under ambient condition [39].

Ramayya et al. [40] revealed Aldol condensation reaction of acetaldehyde can be catalyzed by OH^- generated from high temperature water. Even intramolecular Aldol condensation can also be catalyzed by diluted NaOH, but the reaction is inhibited after adding H_2SO_4 [41].

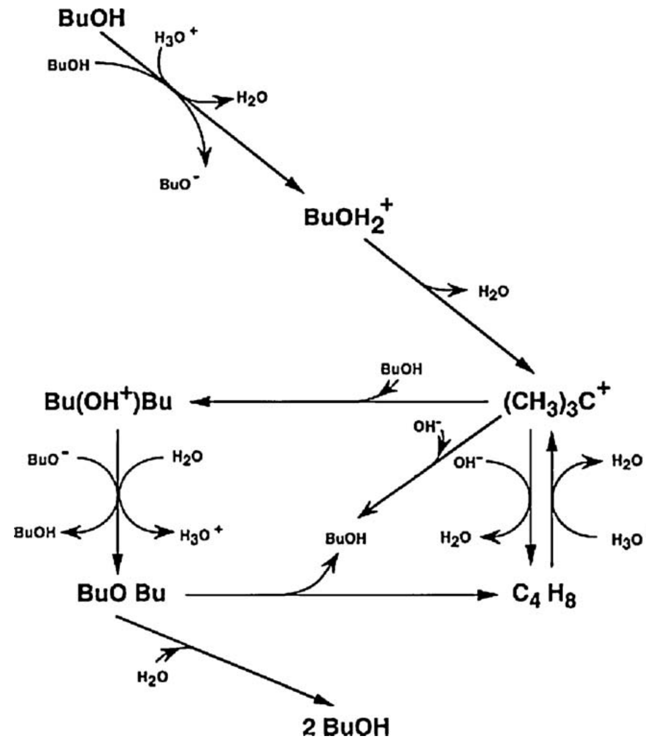


Fig. 4. Acid catalyzed reactions of *tert*-BuOH in HTW [37].

3. Catalytic supercritical water gasification

In the past 20 years, the U.S. Pacific Northwest Laboratory, Hawaii Natural Energy Institute, Foschungszentrum Karlsruhe in Germany, National Institute for Resources and Environment in Japan and other research institutions have had some in-depth researches on the hydrogen production by SCWG of some organic compounds without catalysts. Their studies covered some typical model compounds, such as glucose [25,42–46], methanol [47,48], cellulose [49–52], lignin [51,55] and some real biomass compounds [44,53,54,56–58], organic waste/water [59–61]. As successful demonstrations accumulated, detailed reaction mechanism, kinetics and thermodynamics have built a solid foundation for subsequent investigations.

However, to increase the selectivity of hydrogen production, high activation energy is needed for the reaction without catalysts. The high costs of equipments and operation have undoubtedly become the biggest obstacle to the development of this technology. So much attention has been focused on the research of catalytic supercritical water gasification. We will not discuss the preparation of catalyst in this work, but instead focus solely on the use of

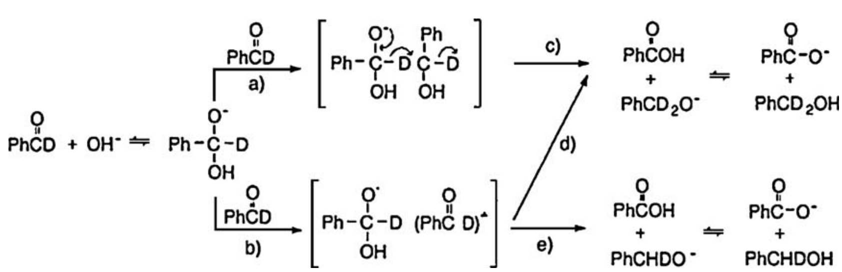


Fig. 5. A postulated mechanism for the disproportionation of benzaldehyde in SCW; (d) D• transfer; (e) H• transfer [35].

Table 1
Summary of the investigations on hydrogen production via catalytic supercritical water gasification in recent 5 years (arranged chronologically).

Target reactant	Catalyst	Reactor type	Experiment condition	Experimental results and comments	Reference
Glucose	Raney nickel and homogeneous organometallic catalysts	Union tee reactor constructed of 316 stainless steel	310–350 °C and 10–21 MPa	Raney nickel was a more effective catalyst compared to homogeneous $Ni(acac)_2$,$Co(acac)_2$, and $Fe(acac)_3$ catalysts.	[70]
Glucose	Ni/activated charcoal	Hastelloy C-276 packed bed reactor	575–725 °C; 28 MPa; feed concentration 0.3–0.9 M; LHSV 6–24 h^{-1}	Ni/AC showed high hydrogen selectivity and stability; Deactivated due to coke deposition at low temperature and also due to sintering of nickel particles.	[69]
Glycerol	Ru/Al_2O_3	Tubular fixed-bed flow reactor	700–800 °C; reaction time <5 s; feed concentration 40 wt%	Ruthenium catalyst showed a high activity for C–C bond scission; Glycerol was completely gasified; H_2 yield decreases with an increase in the feed concentration.	[26]
Lignin	Ruthenium trivalent-salts supported on titanium oxide and charcoal	Sus 316 tube reactor	400 °C; 37.1 MPa; water density 0.5 g/cm^3	The order of gasification activity was $Ru/C \approx Ru(NO)(NO_3)_3/C \approx Ru(NO)(NO_3)_3/TiO_2 > RuCl_3/C \approx RuCl_3/TiO_2$; Small ruthenium metal particles were formed during the lignin gasification in supercritical water.	[71]
Phenol	Ni/C	Fixed-bed reactor heated by fluidized sand bed	350 °C; 20 MPa; 50 h^{-1} LHSV; feed concentration of 2% TOC	The metal load after carbonization was about 47% and surface area was 178 m^2/g; No effect of carbonization time on particle size was observed; Conversion or activity decreased as particle size increased.	[73]
Lignin	Ru/TiO_2	316 stainless steel bomb reactor	400 °C; 0.1 g of lignin; 5.0×10^{-4} g of elemental sulfur; 7.4×10^{-5} mol of metal in catalyst; 0.50 g/cm^{-3} water density	The gas yield decreased with the amount of sulfur added; the sulfur species which poisoned the ruthenium sites were found to be ruthenium sulfide, ruthenium sulfite, and ruthenium sulfate.	[67,68]
Lignin and 4-propylphenol	Ru/TiO_2, Ru/C, Ru/Al_2O_3, Rh/C, Pt/C, Pt/Al_2O_3, Pd/C, Pd/Al_2O_3, Ni/Al_2O_3	316 stainless steel tube bomb reactor	400 °C; water density 0–0.5 g/cm^3	Decomposition to low-molecular weight compounds in the lignin gasification was enhanced by increasing the water density (4-propylphenol is not); Gasification of the low-molecular weight compounds was accelerated over metal catalysts.	[66]
Methanol	In situ generated copper nanoparticles	Stainless steel 316 tubular reactor	700 °C and 27.6 MPa; reaction time<1 min;	The concept is successfully demonstrated for the production of hydrogen from methanol via copper catalysis in supercritical water; The generated nanoparticle surface is highly catalytic, and reforms methanol in about 15 s; Such scheme is also suitable for sulfur-containing feeds.	[64]
Lignin	Ni/MgO	Stainless steel tube bomb reactors	250–400 °C; water density 0.3 g/cm^3	The amount of gases produced increased with an increase in nickel loading on magnesium oxide; MgO decomposed lignin to reactive intermediates and nickel promoted reaction between intermediates and water to form gases; Water density affected the reaction kinetics.	[65]
Methanol	Ni catalyst	Quartz tube	500 and 550 °C; methanol 10 wt.%; fluid density 0.079 g/mL	The conversion rates are greatly increased by added Ni catalyst; Ni metal is subject to deactivation with repeated use.	[63]
Glycerol, glucose and wood	Ru/TiO_2	Quartz capillary reactor	450–700 °C; 5–50 MPa; feedstock 1–20 wt%	Complete conversion of solutions with 1–17 wt% glucose is achieved by adding a 3 wt% Ru/TiO_2 catalyst.	[72]
Methanol	Wall of the reactor made of Inconel 600 (73% Ni, 18% Cr, and 9% Fe), K_2CO_3, KOH	Tubular reactor	700 °C; 27.6 MPa	The reactor made of Ni–Cu tubing minimizes the formation of CH_4; Methanation can also be reduced with the addition of K_2CO_3 or KOH in the aqueous methanol feed.	[47]
Cellulose	Ru/C, Pd/C, CeO_2 particles, nano-CeO_2 and nano-$(CeZr)_xO_2$	140 ml, high-pressure autoclave	650 °C; 35 MPa; 10 wt% cellulose or sawdust	Catalytic activities were Ru/C > Pd/C > nano-$(CeZr)xO_2$ > nano-CeO_2 > CeO_2 particle in turn.	[62]

catalysts to bring about chemical transformations in SCWG process. The literatures reviews with regard to the research of CSCWG in the past 5 years are listed in the Table 1.

3.1. Homogenous catalyst

Catalytic effect of alkali metal catalysts (Na_2CO_3, $KHCO_3$, K_2CO_3, NaOH, etc) on SCWG of biomass has been confirmed by many open literatures. Main characteristic of this catalyst is to improve the water-gas shift reaction.

Kruse et al. [23] reported the catalytic action of KOH on SCWG of pyrocatechol. When the content of KOH increases from 0 to 5%, the smallest yield of CO can be obtained and the production of H_2 and CO_2 increases, which is due to the catalytic effect on water-gas shift reaction in the process by adding KOH. Compared with KOH, LiOH has similar activity on the gas-phase composition but to a smaller extent. Garcia Jarana et al. [74] evaluated the catalytic effect of KOH on SCWG of industrial organic waste. The study shows that the water-gas shift reaction is accelerated by adding KOH. Formic acid is presumed to be the intermediate product in the reaction process, and the production of H_2 and CO_2 is due to decomposition of formic acid.

$$CO + H_2O \leftrightarrow \text{“HCOOH”} \leftrightarrow CO_2 + H_2 \quad (2)$$

The catalytic effect of NaOH was also realized by Watanabe et al. [33]. The yield of CO was inversely proportional to the OH^- concentration, which indicates that HCHO reactions are governed by the OH^- concentration. Their research group conducted another CSCWG experiment on *n*-hexadecane and lignin with NaOH (400 °C, 30 Mpa). The addition of NaOH makes the output of H_2 4 times more than that of being without NaOH. The production of coke is also effectively inhibited [96].

In the study of Ru/TiO_2 catalytic properties on SCWG process, Kersten et al. [72] found that adding Na^+ or K^+ cations as an assistant can promote the water-gas shift reaction, but do not affect the carbon conversion rate.

Yanik et al. [5] employed K_2CO_3 and Trona ($NaHCO_3{\cdot}Na_2CO_3{\cdot}2H_2O$) catalysts for the CSCWG research of some real compounds such as lignocellulosic materials (cotton stalk and corncob) and the tannery waste. The results show that H_2 yield increases significantly when the catalysts are used. The catalytic effect of K_2CO_3 is attributed to the formation of formate ($HCOO^-K^+$) salt in the reaction pathway [75,76]:

$$K_2CO_3 + H_2 \rightarrow KHCO_3 + KOH \quad (3)$$

$$KOH + CO \rightarrow HCOOK \quad (4)$$

Hydrogen is obtained by reacting of formate with water.

$$HCOOK + H_2O \rightarrow KHCO_3 + H_2 \quad (5)$$

The catalytic cycle is completed by the formation of CO_2 and K_2CO_3.

$$2KHCO_3 \rightarrow H_2O + K_2CO_3 + CO_2 \quad (6)$$

The overall reaction (2) is obtained by the integration of the above formulas.

It is clear that K_2CO_3 could change the reaction pathway to accelerate water-gas shift reaction, thus reduce the activation energy of reaction process. Alkali catalysts are important to achieve high hydrogen yield, but may cause corrosion, plugging or fouling [76].

3.2. Heterogeneous catalyst

Compared with the homogeneous catalysts, heterogeneous catalysts have the advantages of high selectivity, recyclability, environment-friendly, etc. So it has become a research hotspot in this field.

3.2.1. Transition metal catalyst

3.2.1.1. Nickel catalyst. The cost of nickel catalyst is relatively low, and it has been applied extensively to many petrochemicalindustries. Based on the previous theory on Nickel catalyst in other chemical processes, many researchers introduced it into supercritical water gasification reaction system to get a better understanding of its hydrothermal activity and stability. Most studies found that the conversion of biomass can be accelerated by Ni catalyst, but both Ni catalyst itself and its support are unstable. Sintering and deactivation are unavoidable in the reaction process.

Elliott [77] did exploratory work on the evaluation of catalysts for hydrothermal gasification. They noted that many reactive metal catalysts including Ni are available to improve the gasification reaction of biomass under supercritical even sub-

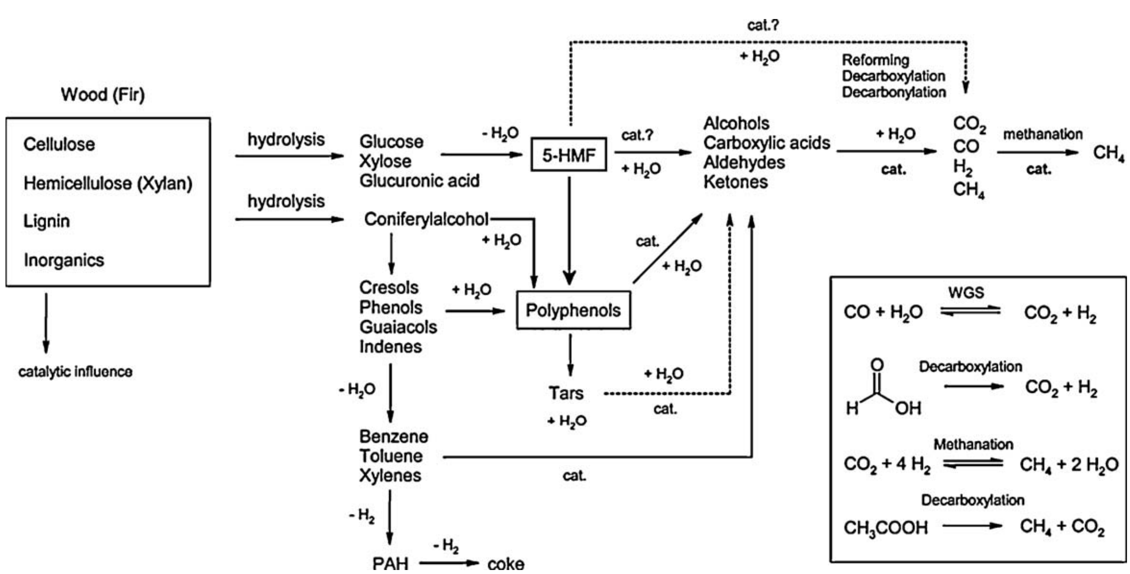


Fig. 6. Simplified reaction network for the hydrothermal gasification of woody biomass. (The term “cat.” designates reaction pathways influenced by the presence of a catalyst, whereas the term “cat.?” denotes pathways that are only assumed to be promoted by a catalyst.) [79].

critical water condition. Their research shows that Ni catalyst is inevitably limited by its life performance (<100 h). The physical and chemical structure of catalyst support greatly changes at hydrothermal condition. The Ni crystallite sinters in both batch and continuous-flow experiments [78].

Waldner et al. [79] have offered an insight into the catalytic effect of Raney Ni for woody biomass SCWG under the operating condition of 300–410 °C and 12–34 MPa. If the reaction time is sufficient (90 min), complete gasification can be obtained, whereas the catalyst surface is covered with some carbon deposit. Presumed catalytic reaction path is shown in Fig. 6.

Ni catalyst also has high activity in the CSCWG processes for many kinds of real compounds (lignin, cellulose, etc). However, inactivation is unavoidable due to the adsorption of intermediate products on the catalyst surface in the process [80].

Furusawa et al. [81,82] employed Ni/MgO catalyst for CSCWG of lignin. They found that the carbon yield of gas products is increased with the increase of Ni metal surface area. 10 wt% Ni/MgO (873 K) shows the best catalytic performance (carbon yield 30%) under reaction condition tested. Additionally, Minowa et al. [83] emphasized the importance of Ni catalyst to steam reforming reaction and methanation reaction. In the subsequent article, they considered that the different support may have different effects on activity of Ni catalyst [84].

Dileo et al. [85] used nickel wire added quartz tube as a reactor (Fig. 7) to catalyze the hydrothermal gasification of guaiacol and phenol (400–700 °C). Nickel does not affect the conversion of guaiacol to phenol and o-cresol, but it significantly changes the gas product compositions. Conversion rate of phenol is 68% after 1 h reaction time, whereas 100% conversion rate can be achieved with catalyst after only 10 min.

The carbon based nickel (Ni/C) catalyst also shows a high catalytic activity in hydrothermal condition [86]. The Ni/C catalyst was prepared by ion exchanging Ni ions with the ion exchangeable sites in an ion exchange resin followed by carbonization of the resin. 170 m^2/g of high surface area can load up 47% of the effective Ni content. SEM image of the catalyst prepared is shown in Fig. 8. Following this work, subsequent evaluation on the effect of carbonization temperature on the nickel crystallite size of Ni/C catalyst for catalytic hydrothermal gasification of organic compounds was accomplished by the group. The conclusions are summarized in the Table 1.

In order to improve the performance of nickel catalyst, Elliott et al. [87] attempted to add trace element such as Cu, Ag, Sn and Ru in the Ni catalyst. The results showed that Ru is of some help to increase the activity of Ni catalyst. Moreover, its longer life performance is proved by continuous tests in laboratory over 6 months.

3.2.1.2. Ruthenium catalyst. Ruthenium is a very active catalyst for low temperature catalytic gasification. Low metal loadings can still produce highly active catalysts [87].

Byrd et al. [89] evaluated the Ru/Al_2O_3 catalyst via glucose CSCWG experiment. In this report, the addition of catalyst can not only improve conversion rate and H_2 yield, but also inhibit CH_4 production. In the subsequent investigation of glycerol CSCWG [26], as shown in the Table 1, this hypothesis was also in consistent with the high activity of Ru/Al_2O_3 for C–C bond scission. The catalytic mechanism can be presumed: oxygenated compounds containing hydroxyl groups adsorb to the catalytic Ru surface predominantly through one or more oxygen atoms. First the reactant undergoes dehydrogenation on the catalyst surface, followed by subsequent cleavage of C–C or C–O bonds. Cleavage of C–C bonds leads to synthesis gas which is subjected to the water-gas shift reaction and possible methanation reaction, while cleavage of C–O bonds gives organic acids and alcohols. BET analysis shows that the catalyst undergoes morphological change during the reaction process. The similar phenomenon is also found in Osada et al.'s experiment [88]. After 180 min reaction, the Al_2O_3 supports transfer from γ to α crystal form and part of Ru metal dissolves in the water.

High H_2 selectivity of Ru catalyst was shown in the report of CSCWG experiment of lignin and glucose [90]. At low temperature (400 °C), intermediate compound formaldehyde is decomposed to CH_4, CO_2 and H_2 rapidly if being catalyzed. On the other hand, without catalyst, formaldehyde is converted to methanol and CO_2. Sato et al. [91] compared variety of heterogeneous catalysts for CSCWG and found that the activity order is $Ru/\gamma\text{-}Al_2O_3 > Ru/C > Rh/C > Pt/\gamma\text{-}Al_2O_3$, Pd/C and $Pd/\gamma\text{-}Al_2O_3$.

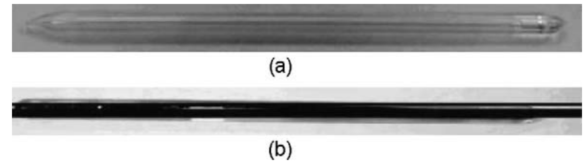


Fig. 7. Quartz reactors (a) before and (b) after SCWG of guaiacol [85].

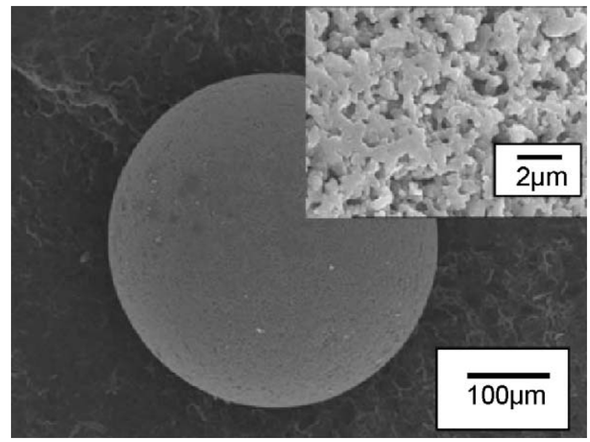


Fig. 8. SEM image of the catalyst prepared [86].

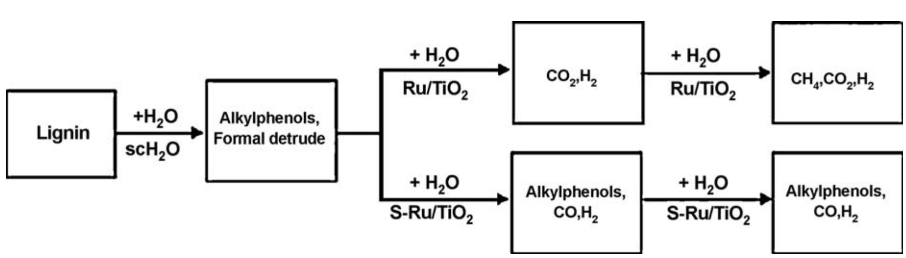


Fig. 9. Reaction pathway of lignin gasification over a supported ruthenium catalyst containing sulfur in supercritical water [68].

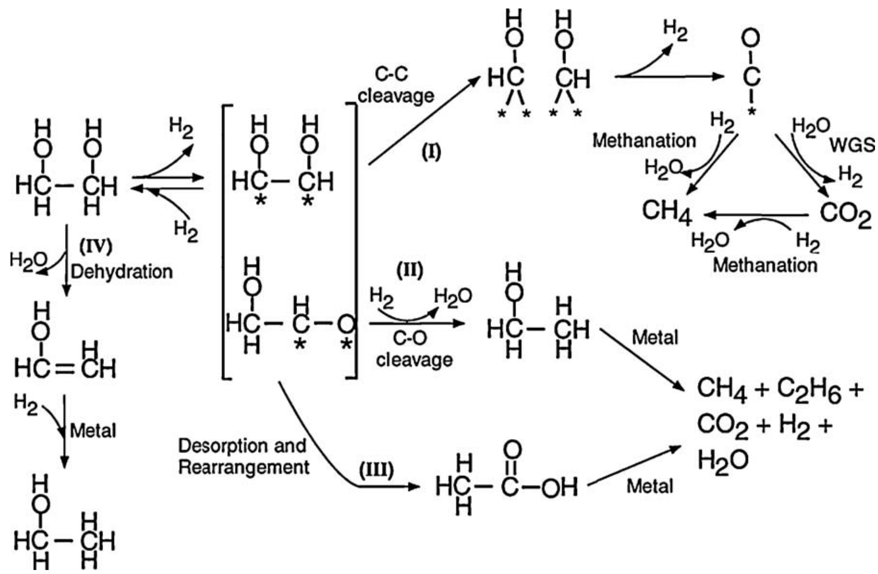


Fig. 10. Reaction pathways and selectivity challenges for production of H_2 from reactions of carbohydrates with water (* represents a surface metal site) [94].

It is worth mentioning that Ru catalyst poisoning is usually caused by trace amount of S which can exist in Ru/C catalyst in the form of $S^{2-}$and $SO_4{}^{2-}$ [67,68]. The reaction pathway with regard to ruthenium catalyst poisoning is shown in Fig. 9. Waldner et al. [92] also noted that adding trace of Na_2SO_4 can lead to catalyst poisoning.

3.2.1.3. Other metal catalyst. Davda and co-worker's [93] finding established that Pt-based catalysts show high activity and good selectivity for the production of hydrogen from sugars and alcohols at low temperature aqueous-phase reforming reactions, and the improvements are necessary to render the process useful. They compared performances of different active metal loading on SiO_2 whose order is $Pt{\sim}Ni > Ru > Rh{\sim}Pd > Ir$ [94]. The Reaction pathway and selectivity challenges for production of H_2 from reactions of ethylene glycol with water is shown in Fig. 10.

ZrO_2 is a typical acid-base catalyst whose structure is mixture of monoclinic crystal and tetragonal crystal. The acidity is decided by the structure itself [95]. After SCW reaction, ZrO_2 transforms into pure monoclinic crystal system which is stable in SCW. Watanabe et al. [96,97] reported the catalytic activity of ZrO_2 for SCWG of glucose and lignin. They found that ZrO_2 not only inhibits CH_4 production but also increases H_2 yield. Yet the catalytic effect is much less than that of NaOH.

3.2.2. Activated carbon catalyst

Activated carbon is another catalyst with great potential for hydrothermal reactions. One of its principal advantages is high catalytic activity. Besides, the secondary pollution is not likely to be caused by dissolved metal from the metal catalysts mentioned above.

Activated carbon such as spruce wood charcoal, macadamia shell charcoal, coal activated carbon and coconut shell for CSCWG process of organic feedstocks was probably the first evaluated by Matsumura and co-workers [27]. The results show that activated carbon not only increases carbon gasification efficiency, but also improves water-gas shift reaction and methanation reaction. However, deactivation on carbon gasification occurred after 4 h and water-gas shift reaction occurred after 2 h. Vortex at the entrance of the reactor may help to increase the conversion rate. The team went on to look at the performance of activated carbon catalyst. They presumed that the reaction pathway should include adsorption of a reactant or an intermediate onto the carbon surface, which is likely to be a significant effect on the catalytic performance of the carbon [98].

Antal et al. [99] found that the biomass laden gel can be steam reformed over a carbon catalyst to a gas composed of hydrogen, carbon dioxide, methane, carbon monoxide, and traces of ethane. More complicated real biomass could decrease the reaction rate.

3.2.3. Catalysis of reactor wall

As most of the supercritical water reactor materials are made by the alloy, the metal on inner wall of the reactor will definitely have an impact on the reaction course. Inconel and "new" Hastelloy were thought to be effective on water-gas shift reaction, but "corroded Hastelloy" wall only catalyzed the decomposition of acetic acid [45]. Lee et al. [25] revealed that Hastelloy C-276 has a wall effect to increase H_2 yield efficiency. Boukis et al. [48] studied a reforming reaction of methanol with supercritical water in a tubular flow reactor made of Inconel 625. They suggested that the heavy metals of the inner surface of the reactor have a significant influence on the conversion and the composition of the reaction products. This catalytically active surface could accelerate both methanol decomposition and the water-gas shift reaction. The catalytic activity can maintain more than 1000 h of operating time. Gadhe and Gupta [47] examined that SCWG are catalyzed by the wall of the tubular reactor made of Inconel 600, which is an alloy of Ni, Cr, and Fe. The main conclusions are listed in Table 1.

4. Conclusions

Supercritical water gasification is a promising method of hydrogen production from biomass. Supercritical water is the best reaction medium for biomass with high water content. Physicochemical properties of supercritical water are greatly different from gas and liquid at normal condition, which makes it possible not only to take part in the reaction as a reactant but also to affect the reaction pathway as a catalyst. But how to reduce the activation energy and moderate the violent reaction condition have become the pressing problems we have to deal with. It is available to overcome these shortcomings by adding catalysts which are suitable for hydrothermal reaction.

According to this summarization, the catalysts used in previous researches can be classified as alkali metals, transition metal (including "wall" effect) and activated carbon catalyst. During the processes, alkali metal catalyst can effectively improve the water-

gas shift reaction, but may cause corrosion, plugging or fouling of equipment. For transition metal catalyst, such as Ni, Pt, Ru and Rh, most studies suppose that they improve the reaction by accelerating the steam reforming reaction, methanation reaction and cleavage of C–O and C–C and so on. In addition, activated carbon catalyst is also effective during water-gas shift reaction and methanation reaction. It is concluded that these catalysts can effectively increase conversion rate, hydrogen selectivity and decrease the activation energy in SCWG reaction. On the other hand, dozens of studies have confirmed the instability of the most catalysts. Besides, destruction of their support is also observed.

Continuous research is necessary to get a deeper understanding in the chemistry which can be mastered with the development of efficient and stable catalysts. Given the opportunities that catalysis in SCWG provides for advances in green chemistry/engineering and sustainable energy, one can expect even more research and development activity in this growing field. If the good cost performance can be provided, this technology holds great potential to be large-scale commercialized in the future.

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